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PATENT SPECIFICATION

NO DRAWINGS

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COMPLETE SPECIFICATION

High Temperature Protective Coating

We, ESSO RESEARCH AND ENGINEERING COMPANY, a Corporation duly organised and existing under the laws of the State of Delaware, United States of America, of Elizabeth, New Jersey, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention is directed to single application high temperature inorganic protective coatings utilizing a lithium-sodium silicate vehicle. In its more specific aspects, the present invention is concerned with high temperature coating compositions comprising a lithium-sodium silicate vehicle, a silica sand and a metallic or semi-metallic pigment.

The present invention may be briefly described as high-temperature coating compositions made up of an aqueous vehicle of a lithium-sodium silicate solution, the lithium-sodium silicate being derived from lithium hydroxide sodium hydroxide and a silica-containing material in amounts sufficient to provide a molar ratio of lithium oxide:sodium oxide:silicon dioxide within the range from 0.50 to 1.00; 0.05 to 0.25; 2.5 to 5.0; a silica sand; and a metallic or semi-metallic pigment selected from the group of aluminum, nickel, stainless steel and other iron alloys having melting points above 1200°F. In its more specific aspects, the invention is concerned with the addition of certain other materials such as zinc dust and color pigments to provide cathodic protection and specially adapted coating compositions.

The designation "high temperature coating" is applied to a protective inorganic coating designed for service on metal surfaces which may be operated continuously or for short periods at temperatures in excess of 900°F. Heretofore, the normal industrial coatings were either totally destroyed or rendered in-

effective when applied to a surface which had an operating temperature in excess of 900°F. It should be pointed out, however, that the recommended operating temperatures of the coating cannot extend the operating or service temperature recommended for the metal to which it is applied. Accordingly, for a cold-rolled carbon steel the recommended service temperature is about 1000°F., and while the coatings of the present invention may withstand temperatures in excess of 1000°F., the coatings can be no better than the surfaces to which they are applied. The coatings of the present invention have been found suitable for service to temperatures of at least 1750°F. when applied to other than a mild carbon steel. While the coatings of the present invention are designated as high-temperature coatings, they are effective and useful on metal surfaces at temperatures considerably below 900°F.

The present invention is also concerned with the selection of proper pigmentation to formulate satisfactory inorganic high temperature coatings. The selection of the pigment must take into consideration the following: high temperature stability, film flexibility, corrosion resistance, and desirable color. The high temperature coating compositions of the present invention were formulated taking into consideration all of these aspects of the problem.

The lithium-sodium silicate vehicle of the present invention is prepared by adding lithium hydroxide, which is preferably the monohydrate since it is easier to use and is commercially available, sodium hydroxide and silica-containing materials, such as silicic acid and silica gel, to water while agitating the same, following which the admixture is heated while continuing the agitation thereof to a temperature within the range of 75°C. to 250°C. for a sufficient length of time to form a mixture of lithium and sodium silicates. The

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sodium and lithium hydroxide and silicate-containing material are used in amounts sufficient to provide a molar ratio of lithium oxide to sodium oxide to silicon dioxide within the range from 0.50 to 1.00; 0.05 to 0.25; 2.5 to 5.0, respectively, following which the admixture is cooled to a temperature within the range from about 20° to about 30° at which temperature any solids go into solution and form an aqueous solution thereof.

The lithium-sodium silicate vehicle may be further described in another manner, i.e., the sodium and lithium hydroxides and silica-containing material are used in amounts sufficient to provide a molar ratio of lithium oxide to sodium oxide within the range of 20/1 to 2/1, and a molar ratio of silicon dioxide to the combined lithium oxide and sodium oxide within the range of 2.0/1 to 9.1/1. The same lithium-sodium silicate vehicles are described by the foregoing, and only the manner of expressing the same differs. As is known to the art, the use of the oxide ratios is a means for defining silicate solutions and does not mean that the oxides exist as such. The lithium-sodium silicate vehicles of the present invention are in most instances colloidal in nature.

The preferred lithium-sodium silicate vehicles of the present invention are further characterized as follows: The vehicle has a solids content of between 25% and 30% by weight. A vehicle prepared by the preferred method has a total solids contents of about 26% to about 27% by weight. The vehicle has a viscosity of between 30 to 40 centipoises, the preferred vehicle having a viscosity of between about 36 to about 37 centipoises. The specific gravity of the vehicle may range from 1.185 to 1.2. A preferred specific gravity for the vehicle is about 1.194 to about 1.195.

The addition of the silica sand to the high-temperature coating compositions of the present invention is to provide film flexibility. By film flexibility is meant that the coating has the ability to contract and expand rapidly as the surface to which the coating is applied undergoes wide temperature variations. The silica sand found suitable for the present invention may be characterized as a sand of small particle size which has the constituency of powder in contrast to a sand having a highly irregular crystalline structure. The preferred sand is commercially available 325-mesh silica sand which means a sand having a size such that it passes through a 325-mesh Tyler screen. However, a sand suitable for the present invention may have a particle size within the range such that between 90 per cent to 100 per cent will pass through a 325-mesh Tyler screen. While the sand and the vehicle alone will give an excellent coating as far as film flexibility is concerned, it has no corrosion protection property; and accordingly, rusting underneath the film would eventually

occur causing such a coating to fail.

It has been found that the addition of a metallic or a semi-metallic pigment, when added to the vehicle of the present invention together with the silica sand, produces a coating having high temperature stability and exhibiting sufficient corrosion resistance for a practical composition. The metallic pigments which are suitable for the present invention include aluminum, nickel, stainless steel and iron alloys having melting points above about 1200°F. More particularly, the metallic or semi-metallic pigments should have a melting point about 250°F. above the maximum service temperature which the coating is to be subjected. The addition of the metal pigments such as metallic aluminum or metallic and semi-metallic nickel provides coatings having excellent temperature, shock and heat resistance as well as exhibiting a certain degree of resistance to corrosion.

By the term semi-metallic pigments, it is meant that the pigments are composed of particles having about 50% by weight of the metal around a core of about 50% by weight of either talc or mica. The metal pigments which are preferred are capable of withstanding the temperatures under which the coating will be subjected; that is, temperatures of at least 1650°F. and will not melt or discolor the coating. The metallic pigments have a particle size such that approximately 95 weight per cent will pass through a 325-mesh Tyler screen.

In a corrosive atmosphere or to provide a coating having good corrosion protection, zinc dust may be added to the coating compositions of the present invention. This finding was unexpected since the zinc dust was otherwise found unsuitable as a metallic pigment since zinc melts at about 786°F. The addition of the zinc to the high temperature coating compositions of the present invention which include the vehicle, the sand, and the metal pigment unexplainably will provide excellent high-temperature coatings. The zinc has a particle size between 2 to 50 microns in diameter and preferably the particles have a size within the range of 5 and 20 microns in diameter. The zinc may be added in an amount from 1% to 60% by weight, and the coatings will display increasing corrosion resistance to the metal, especially carbon steel, as the amount of zinc is increased.

It has also been found that even though the coatings will become essentially dry in air in 30 to 45 minutes, the corrosion resistance of the zinc-enriched coatings can be enhanced by heating the metal surface to which the coatings are applied to a temperature up to about 350°F. The heating of the surface does not mean that curing is required for these coating compositions; however, the heating of the metal surface will give an improved corrosion resistance to the coating. The heating may be

accomplished as the metal is brought to operating conditions.

In addition to the coating components previously discussed, certain other materials, generally referred to as pigments, may be added singly, collectively, or in various combinations to impart certain desired properties to the coatings. Several of these "pigment additives" and the desirable characteristics they appear to provide to the coatings of the invention are as follows:

(1) *Inorganic Ceramic Pigments* (metallic oxides which alone or in various combinations yield desired colors) — provide a means of giving these coatings a variety of high temperature-resistant colors. Examples of the metallic oxide pigments are cobalt/aluminum, cobalt/chrome, cadmium, and cadmium/

aluminum. The preferred pigments are those commonly used in tinting ceramics.

(2) *Zinc Oxide Pigment* — enhances the abrasion resistance and over-all "smoothness" of the coating surface by contributing comparatively minute (0.1—1 micron diameter) particles to the coating formulation.

(3) *Aluminum Silico-Phosphate Pigment* — performs the same function as Zinc Oxide.

(4) *Titanium Dioxide Pigment* — in addition to enhancing the abrasion resistance of these coatings, titanium dioxide contributes its excellent hiding properties (brought about by a very high index of refraction) to these coatings.

The preferred coating compositions of the present invention are formulated in accordance with the following general formulas:

	Lithium-sodium silicate vehicles	20—45 wt. %
	Sand	15—60 wt. %
	Zinc Dust	0—60 wt. %
	Metallic Pigment	1—10 wt. %
	Pigment Additives	max. 5 wt. %
	Inorganic Ceramic Pigment	1—2 wt. %

The weight per cent of the sand and zinc are selected such that the more zinc used the less sand is used. However, when the weight per cent of sand is higher, then a higher weight per cent of vehicle must be used to keep all solids in solution.

The coating compositions of the present invention are applied to metal surfaces which have been prepared by commercial sandblasting techniques. It is preferred that the metal surfaces be sandblasted to white metal prior to coating. The coating compositions are applied to the surfaces by brushing, rolling or spraying a dry film of about 2 to 12 mils in thickness. A preferred dry film thickness is about 3 to 6 mils. To obtain the preferred dry films, a wet film of about 6 to 10 mils of the coating compositions is applied to the white metal surface.

The lithium-sodium silicate solution without the addition of any additive materials may be formed in the following manner:

EXAMPLE I

Water, silica gel, lithium hydroxide and sodium hydroxide are charged into a stainless steel pressure vessel equipped with an agitator. During the initial mixing of these ingredients, evolution of heat raises the temperature of the contents to 50° to 55°C. The reactor is then sealed and the temperature of the reactants, under a continual agitation, is raised

to 150°C. for a period of time, which may vary from 30 to 90 minutes. After the vessel reaches about 150°C. and about 70 psi pressure, the contents are slowly cooled at a rate of 0.61°C. to 1.83°C. per minute. This will result in a temperature drop from 150°C. to about 95°C. within 30 to 90 minutes. This completes the initial part of the reaction which forms the solid sodium-lithium silicates.

The second part of the operation (below 95°C.) requires a longer period of time in order to effectively dissolve the solid silicate at the lower temperatures. The reduction of the temperature of the reactor contents from 95°C. to 40°C. is at a rate of 0.37°C. to 0.146°C. per minute and is accomplished in 150 minutes to 240 minutes. The last temperature drop from 40°C. to 25°C. may be conducted over a period of 60 to 120 minutes and a cooling rate of 0.25°C. to 0.125°C. per minute.

Depending on the amount of water used, the vehicle may be used in different solid ratios, i.e., the total solids of the vehicle may vary from 10% to 45% by weight, preferably the solids content is between 25% to 30% by weight.

EXAMPLE II

A vehicle was prepared in the manner similarly described in Example I except it was made of the following ingredients:

	Sodium hydroxide	8 parts by weight
	Lithium hydroxide monohydrate	34 parts by weight
	Silica gel	126 parts by weight
	Water	400 parts by weight

- This vehicle may be described as 0.75 Li₂O: 0.25 Na₂O:4.5 SiO₂ or having a molar ratio of Li₂O to Na₂O of 3/1 and a molar ratio of SiO₂ to the combined Li₂O and Na₂O of 4.5/1. The vehicle had a total solids content of about 27 weight per cent but may vary between 26 to 28 per cent. The viscosity of the vehicle was 36 to 37 centipoises, and the specific gravity was about 1.194 to 1.195.
- EXAMPLE III
- A composition was prepared using the following ingredients:
- | | |
|-------------------------|-------|
| Vehicle from Example II | 40.8% |
| 325-mesh sand | 54.2% |
- Application of this composition to a sand-blasted steel panel indicates a fairly uniform coating which dried in air in about one hour. The steel panel coated with the composition was heated to 1200°F. and immersed in cold water. Upon repeated heating and cooling, the coating showed excellent flexibility characteristics; however, the coating failed when exposed to a 5% salt spray in a salt fog cabinet after only 24 hours due to rusting beneath the film. The composition of this example does not produce a suitable high-temperature coating for normal outside applications, not only because of its failure to prevent corrosion but also because the resulting coating exhibits low abrasion resistance.
- EXAMPLE IV
- A coating composition was prepared using the following ingredients:
- | | |
|---------------------------|-------|
| Vehicle from Example II | 43.1% |
| 316-Stainless steel flake | 9.2% |
| 325-mesh sand | 47.7% |
- EXAMPLE V
- A coating composition was prepared using the following ingredients:
- | | |
|-------------------------|-------|
| Vehicle from Example II | 42.0% |
| Semi-metallic nickel | 9.4% |
| 325-mesh sand | 48.6% |
- The coating compositions of Examples III, IV, and V all withstood temperatures of 1350°F. for two hours. The following table, however, points out the differences with regard to the corrosion resistance of the coating.

TABLE I

Material Tested	Corrosion Resistance* (144 hrs.; 5% Salt Fog Spray)	Abrasion Resistance**	Estimated Maximum Operating Temperature***
Example III	1.0	0.169%	1500 — 1800° F.
Example IV	4.5	0.601%	1500 — 1800° F.
Example V	3.0	0.562%	1200° F.

* Rated on the basis of 10 = perfect, no corrosion
0 = total failure, very severe corrosion

** Percentage weight loss after 500 cycles with Taber Abrader (1000 gm load)

*** Projected on the basis of short-term laboratory exposures (these exposures range from 1 to 2 hours to 70 days)

- The foregoing examples show that the presence of the metallic pigments produces a coating composition wherein the coating formed will have sufficient corrosion and abrasion resistance to produce a suitable coating. Coating compositions such as illustrated by Examples IV and V are suitable for high-temperature applications, especially for decorative applications and where corrosion problems are not severe. These coatings may be used to coat machines, engines and the like which are protected from corrosive atmospheres in some other way than by the coating itself.
- Additionally, coatings of this composition may be used as coatings for ultra-high temperature alloys such as Inconel (Reg. Trade Mark), Austenitic Grade 316 stainless steel, etc., which operate in the ranges of approximately 1000°F. to 1800°F. and are themselves protected from corrosion by their inherent nature. For coating metal surfaces, especially mild carbon steels, which are subject to the weather or other corrosion problems requiring cathodic protection, zinc dust is added to the coating compositions as shown in the following examples.

EXAMPLE VI
A coating composition was prepared using the following ingredients:

5	Vehicle from Example II	37.8 wt. %
	325-mesh silica	35.8 wt. %
	316-Stainless steel flake	6.8 wt. %
	Zinc dust	14.3 wt. %
	Rutile titanium dioxide	5.3 wt. %

Vehicle from Example II	42.2 wt. %	
325-mesh silica	36.4 wt. %	
Semi-metallic nickel	7.0 wt. %	
Zinc dust	14.4 wt. %	15

EXAMPLE VIII
A coating composition was prepared using the following ingredients:

EXAMPLE VII
10 A coating composition was prepared using the following ingredients:—

Vehicle from Example II	37.7 wt. %	
325-mesh silica	25.0 wt. %	
Aluminum flake	2.7 wt. %	
Zinc dust	34.1 wt. %	20

TABLE II

Material Tested	Corrosion Resistance* (300 hrs.; 5% Salt Fog Spray)	% Wt. Loss On Taber Abrader (500 cycles—1000 gm. wt.)	Estimated Maximum Operating Temperature***
Example IV	3.25	0.601%	1500 — 1800° F.
Example V	3.0	0.562%	1200° F.
Example VI	7.25	0.138%	1000 — 1200° F.
Example VII	7.0	0.083%	1000° F.
Example VIII	9.5	0.053%	1200° F.

* Rated on the basis of 10 = perfect, no corrosion
0 = total failure, very severe corrosion

*** Projected on the basis of short-term laboratory exposures (these exposures range from 1 to 2 hours to 70 days)

- 25 The compositions of Examples VI, VII and VIII all went through 10 cycles of heating to 1200°F. and sudden cooling by immersion in room temperature water. This test served to illustrate the excellent thermal shock resistance of these coatings.
- The following coating compositions were prepared to show the effect of the amount of zinc in the composition: 30

Example	Wt. % of Each Constituent						
	IX	X	XI	XII	XIII	XIV	XV
Vehicle from Example II	43.1	41.5	40.1	44.0	38.6	33.2	27.2
325-mesh stand	47.7	44.6	43.1	35.2	30.9	26.5	19.0
316-Stainless steel flake	9.2	8.5	8.2	6.7	5.9	5.3	4.8
Zinc dust	0	5.4	8.6	14.1	24.7	35.0	48.9

- 35 The coating was applied to steel panels of each of the compositions of Examples IX to XV and tested for corrosion resistance and heat resistance. The results are listed in the following table:

TABLE III

Material Tested	Corrosion Resistance* (300 hours)	Estimated Maximum Operating Temperature***
Example IX	3.25	1500 — 1800° F.
Example X	5.0	1400° F.
Example XI	7.0	1400° F.
Example XII	7.5	1000 — 1200° F.
Example XIII	8.0	1000 — 1200° F.
Example XIV	10.0	1100° F.
Example XV	10.0	1000° F.

* Rated on the basis of 10 = perfect, no corrosion
0 = total failure, very severe corrosion

*** Projected on the basis of short-term laboratory exposures
(these exposures range from 1 to 2 hours to 70 days)

As can be seen from the results shown in Table III, the coatings are more corrosion resistant with the addition of increasing amounts of zinc, but the coatings become less heat resistant and tend to discolor when the amount of zinc increases over about 50% at a temperature of 1100°F.

A preferred metallic pigment is aluminum powder. Coating compositions of the present invention using aluminum powder as the metallic pigment may be formulated according to the following formula:

		% by weight
15	Lithium-sodium silicate vehicle	25—40%
	325-mesh sand	15—30%
	Aluminum powder	1—10%
	Zinc dust	30—55%
	Color additive pigments	2—5%

20 Specific examples may be illustrated by the following examples:

	EXAMPLE XVI	
	Vehicle from Example II	31.5%
	325-mesh sand	17.8%
25	Aluminum powder	1.8%
	Zinc dust	48.9%

	EXAMPLE XVIII	
	Vehicle from Example II	29.6%
	325-mesh sand	16.8%
30	Aluminum powder	1.2%
	Zinc dust	49.4%
	Mixture of cobalt and aluminum oxide color pigment	3.0%

35 The coating compositions of Examples XVI and XVII may be considered substantially the same except for the color pigment of Example

XVII which results in a pleasing blue color. Both compositions are characterized by having approximately 50% by weight of zinc dust. The following coating compositions are characterized by having a zinc dust level of approximately 35% by weight.

	EXAMPLE XVIII	
	Vehicle from Example II	37.7%
	325-mesh sand	25.6%
	Aluminum powder	2.6%
	Zinc dust	34.1%

	EXAMPLE XIX	
	Vehicle from Example II	36.8%
	325-mesh sand	22.4%
	Aluminum powder	2.2%
	Zinc dust	34.7%
	Mixture of cobalt and aluminum oxide color pigment	4.0%

WHAT WE CLAIM IS:—

1. A coating composition made up of an aqueous lithium-sodium silicate vehicle consisting essentially of a lithium-sodium silicate solution, said lithium-sodium silicate being derived from lithium hydroxide, sodium hydroxide and a silica-containing material in amounts sufficient to provide a molar ratio of lithium oxide to sodium oxide of 20/1 to 2/1 and a molar ratio of silicon dioxide to the combined lithium and sodium oxide of 2.0/1 to 9.1/1; a silica sand; and a pigment selected from the group consisting of metallic and semi-metallic aluminum, nickel, stainless steel and other iron alloys having melting points above 1200°F.

2. A coating composition according to claim 1 which also contains an inorganic ceramic pigment in the form of a metallic oxide to provide color.

3. A coating composition according to claims 1 or 2 which also contain zinc dust.

4. A coating composition according to claims 1—3 characterized in that it contains

a metallic aluminum pigment having a size such that at least 95 per cent will pass through a 325-mesh Tyler screen.

5. A coating composition according to claims 1—4 characterized in that said lithium-sodium silicate is derived from lithium hydroxide, sodium hydroxide and a silica-containing material in amounts sufficient to provide a molar ratio of lithium oxide to sodium oxide of about 3/1 and a molar ratio of silicon dioxide to the combined lithium and sodium oxide of about 4.5/1, said vehicle has a total solids content of between 25 to 30 weight per cent; said silica sand has a size such that between 90 and 100 per cent will pass through a 325-mesh Tyler screen; and said pigment is selected from the group consisting of metallic and semi-metallic aluminum, nickel, stainless steel and other iron alloys having melting points above 1200°F.

6. A coating composition according to claims 1—5 characterized in that it consists of:

Lithium-sodium silicate vehicle	20—45 wt. %
Sand	15—60 wt. %
Zinc dust	0—16 wt. %
Metallic pigment	1—10 wt. %
Pigment additives	max. 5 wt. %
Inorganic ceramic pigments	1—2 wt. %

7. A coating composition made up of an aqueous lithium-sodium silicate vehicle consisting essentially of a lithium-sodium silicate solution, said lithium-sodium silicate being derived from lithium hydroxide, sodium hydroxide and a silica-containing material in amounts sufficient to provide a molar ratio of lithium oxide to sodium oxide of about 3/1 and a molar ratio of silicon dioxide to the combined lithium and sodium oxide of about 4.5/1, said vehicle having a total solids content of between 25 to 30 weight per cent and being present in an amount between 25 per cent and 40 per cent by weight; a silica sand having a size such that between 90 per cent and 100 per cent will pass through a 325-

mesh Tyler screen and present in an amount between 15 per cent and 30 per cent by weight; and a metallic aluminum pigment having a size such that at least 95 per cent will pass through a 325-mesh Tyler screen and present in an amount between 1 per cent and 10 per cent by weight.

8. A coating composition according to claim 7 which includes zinc dust in an amount between 30 per cent and 55 per cent by weight.

9. A coating composition according to claim 1, substantially as described with particular reference to the Examples.

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